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# PRODUCTION OF BOILER FEED QUALITY WATER FROM WELLHEAD BITUMEN/WATER/MINERAL EMULSION BY USING POROUS MEMBRANES

by

C. Nader*, B.A. Farnand**, and H. Sawatzky**

A study was made of porous membranes for use in the production of boiler feed quality water from bitumen/water/mineral emulsions. Various membrane pore sizes and several materials were investigated. Membranes that resisted fouling were identified, and emulsion destabilization by the removal of polar materials was observed.

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# PRODUCTION D'EAU POUR ALIMENTATION DES CHAUDIERES PROVENANT D'UNE EMULSION BITUME/EAU/MINERAL DE TETE DE PUIT A L'AIDE DE MEMBRANES POREUSES

C. Nader*, B.A. Farnand**, et H. Sawatzky**

## Résumé

On a étudié l'utilisation de membranes poreuses pour la production d'eau, rencontrant les normes d'alimentation de chaudières, provenant d'émulsions bitume/eau/minéral. On a examiné quelques membranes de porosité différente. On a observé la déstabilisation de l'émulsion par l'enlèvement des composés polaires et identifié les membranes résistant à l'encrassement.

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# INTRODUCTION

The amount of water required for enhanced oil recovery (EOR) of heavy oil and bitumen with steam floods and other water dependent fluid methods is so large that it may become the restricting factor for development of some projects (1). Also, methods of EOR and in situ recovery produce stable wellhead oil-in-water (O/W) emulsions which resist conventional treatment and can be processed only at great expense by chemicals or energy intensive treatment units (1-6). Even with existing specialized steam generation facilities the production of steam from product water is difficult and accounts for only a small amount of EOR and in situ steam supply (3, 7-9).

Previous work in our laboratory has demonstrated the possibility of using porous membranes as a physical method of breaking bitumen/water emulsions in a batch process to produce high quality water (10). This report is an extension of the previous work to a quasi-continuous membrane process with analysis of the permeate for boiler feed quality parameters. The emulsion used to demonstrate this was a wellhead bitumen/water/mineral emulsion of approximately 4% bitumen supplied by Texaco Canada Resources Ltd., from a steam flood in situ pilot plant at Fort McMurray, Alberta. This wellhead emulsion is currently treated by adding chemical demulsification agents at elevated temperatures (3). Further processing is concerned with producing low water content bitumen with little emphasis on the product water quality.

The use of porous membranes for breaking O/W emulsions is not unique; trade literature and scientific literature are available (11-14). However, no reports exist on the treatment of bitumen/water emulsions with porous membranes. This could be a result of the unusual properties of the bitumen/water emulsions related to the presence of clay, other minerals, water, and dissolved species including salts. The effect of clay on stabilizing O/W emulsions has been demonstrated by Gewers with Athabasca bitumen by Gewers and he has indicated that this effect is reduced at pH 7 to 8 (6). Broughman reports the density of bitumen and water overlaps at 34°C and 115°C, with water slightly denser between these two temperatures (15). He also reports that this difference is maximized from 65°C to 80°C. With this information, operating conditions for Athabasca bitumen/water/mineral

separations should be at pH 7 to 8 and temperatures from 65°C to 80°C. Although the pH range is acceptable for the membrane used in this work, the temperature range is the extreme of usual membrane practice. The emulsion as supplied was pH 7.

Parameters describing the quality of boiler feed water for several types of steam generation have been summarized by Fulton as shown in Table 1 (9). Although the Thermosludge Generator has lower water quality standards, it also has higher capital and operating costs than a once-through steam generator. For this reason, the once-through generator's standards were considered a test of any water recycle process. Other water standards have been included in Table 1 for comparison.

## EXPERIMENTAL

Unlike the previous work (10), a continuous system for the evaluation of membrane performance was assembled as shown in Fig. 1. When operating with the emulsion, there was considerable difficulty in controlling the operating pressure, which was apparently caused by free bitumen "slugging" through the back pressure control valve. This caused rapid but small variations in the operating pressure which were visually averaged to determine the system's operating pressure. As well, the emulsion was opaque and the rotameter shown in Fig. 1 was not used in the emulsion experiments. For the elevated temperature experiments, no attempt was made to insulate the system from the surroundings, and heat was only applied to the reservoir. Accordingly, the reservoir's temperature was 75°C and the liquid's temperature at the end of the series of cells was 45°C. The latter was considered more significant because of the large amount of tubing and fittings between the reservoir and the first membrane cell.

The experiments were conducted in the following order. First, a pure water permeation (PWP) experiment was performed to determine the PWP rate for each membrane, followed by the replacement of the pure water with KI solution. The permeation rate (PR) of the KI solution experiment was determined for each membrane, and the concentration of KI in the permeate and the reservoir was measured. A function describing the separation is defined as:

$$F = \frac{\text{reservoir concentration - permeate concentration}}{\text{reservoir concentration}} \quad (1)$$

where F is the fraction of separation and is expressed as a per cent.

The second step consisted of replacing the KI solution with the bitumen/water/mineral emulsion. The PR was determined, and the permeate was analyzed for total dissolved solids (TDS), metals (Mg, Ca, Fe), silica, and pH. The feed solution consisted of 2 L of emulsion, and was not adjusted throughout this step. The third step consisted of replacing the emulsion in the reservoir with a new sample and performing the experiment as in the second case, except the temperature was increased to 75°C in the reservoir and 45°C for the membrane cells.

All of these experiments were performed at 1800 kPag operating pressure and with a circulation rate of 0.5 L/min. The pressure drop throughout the cells at this flowrate was less than 30 kPa, and constant operating pressure was assumed.

## RESULTS AND DISCUSSION

The characterization of the membranes is given in Table 2 with typical KI solution experimental results. The degree of separation is considered inversely proportional to the pore size of the membranes. This assigns the cellulose acetate (CA) membrane the smallest pore size, and the nitrocellulose (NC) or the polytetrafluorethylene (PTFE) membranes the largest pore sizes. It should be noted that heat treatment usually reduces the pore size of polymeric membranes. A wide range of pore sizes was made available for this study in order to evaluate membrane facility for the removal of dissolved species from the permeate. The penalty for small pore sizes is reduced permeation rate, although this is mitigated by the "population" of pores which is considered a function of the membrane fabrication method, membrane material morphology, and molecular weight.

The variation of permeation rates (corrected to the equivalent of 25°C operating temperature) with time is shown in Fig. 2 for the two operating temperatures (25°C and 45°C). This figure demonstrates the large

decrease of permeation rate that occurs when the bitumen/water/mineral emulsion is broken on membrane surfaces. The exception to this is the regenerated cellulose (RC) membrane permeation rates. While a slight decrease of permeation rate was observed for the two RC membranes during the 25°C experiment, they did not suffer the drastic decreases observed for the other membranes. This ability of cellulose membranes to resist organic component fouling has been reported elsewhere (16). However, operating at 45°C caused a large decrease in permeation rate for all membranes. Because of this, this temperature is not desirable for the long term use of the membrane types studied.

In general, the appearance of the permeates was clear with varying degrees of amber colour, roughly inversely proportional to the KI solution. There was no detectable odour, and no evidence of sediment even on long standing, although there was evidence of long-term bacterial activity. As well, the permeate supported a large foam formation when it was shaken. More specific analyses are shown in Table 3 and the limits for single pass boiler feed water of Table 1 are included for comparison. In all cases, TDS passes the limits set in Table 1. However, the PTFE membrane exhibited unusual two-phase permeation for the 45°C experiment, and demulsified bitumen could be observed in the permeate as 2- tp 3- mm diam droplets. These phenomena could be the result of the large pore size of the membrane combined with the strong preferential sorption of the bitumen on the PTFE surface.

To confirm that organic material in the permeate was not bitumen i.e., hydrocarbons, for cases other than the PTFE membrane, attempts were made to extract the permeate with toluene. There was no evidence of transfer of the coloured material from the aqueous to the organic phase, nor was there any visible residue left by the evaporation of the toluene phase. To further evaluate the organic material in the permeate, it was extracted with ethyl acetate at reduced pH and evaporated on to NaCl plates (17). Infrared analysis showed material similar to that observed by Poirier (17), and was very similar to the infrared spectra of naphthenic acids (Eastman, "Practical" Grade). Infrared analysis of toluene extracted emulsion showed much different material, mainly saturated hydrocarbon structures as well as some polar groups. This analysis was also similar to that reported by Poirier (17).

An unexpected effect was the separation of the emulsion in the resevoir to form two layers: bitumen rich and water rich. The bitumen-rich layer floated as scum on the surface. This layer was retrieved and analyzed for water content by Dean and Stark analysis. The bitumen content was 23% at 25°C and 35% at 45°C. Since this effect was unexpected, the retrieval of the bitumen-rich layer may have incorporated water-rich emulsion into it. No attempt was made to measure the rate of accumulation of this layer. However, the instability of the remaining water-rich emulsion was evident as it continued to break down at room temperature to a very dark bitumen-rich layer on the bottom and sandy/muddy brown water layer with a visible large particle. The original emulsion as received did not segregate to the same extent.

On this basis, it is possible that the polar material observed in the permeate was the stabilizing agent for the bitumen/water/mineral emulsion, and its removal would cause this segregation. This effect has been described by Gewers (6), where the increase in stability of Athabasca bitumen is enhanced by the presence of asphaltenes and other polar material, as observed by infrared analyses.

Analysis of the concentration for selected metals in the permeates is reported in Table 3. Low concentrations of these metals were observed with the exception of Si, although CA met the requirements of Table 1 and most of the others were close to this requirement. For Fe, the detection limit for the ion inductively coupled plasma (ICP) analysis is 0.118 ppm, which is greater than the limit given in Table 1. Although the exact concentration of Fe for these permeates was not measured, it is at least in the same range as the limit in Table 1; it is assumed that further refinement of the process will give satisfactory levels.

## CONCLUSIONS

The use of porous membranes can be considered for the production of boiler feed quality water from bitumen/water/mineral emulsion obtained from the Texaco Athabasca site. The use of a continuous membrane process is possible as demonstrated by this work. An associated difficulty caused by the emulsion is membrane fouling, although the RC membranes do not foul to the same extent.

Depending upon the water quality and the end use of the product water, the membrane pore size can be modified to give a desired performance and several ranges were demonstrated in this work An unexpected benefit is the removal of small amounts of permeate that causes the emulsion to destabilize and break down to water-rich and bitumen-rich phases, which would aid further processing. This effect appears to be related to the removal of polar material by the permeate.

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Table 1 - Water quality objectives for steam generation and other uses (9)

| Parameter | Once-through steam generator[d] | Thermosludge generator[a] | Deep well disposal [b] | Irrigation | Cooling water make-up |
|---|---|---|---|---|---|
| Total hardness, mg/L as $CaCO_3$ | 0.5 | 100-2000 | | | c |
| Silica, mg/L | 50 | 10-250 | | | c |
| Oil, mg/L | 1 | 50-1000 | 20 | 5 | 1 |
| TDS, mg/L | 8000 | 1000-50000 | | 1000 | - |
| Suspended solids, mg/L | 0 | 10-500 | 5 | | d |
| Dissolved $O_2$, mg/L | 0.04 | - | | | - |
| Iron, mg/L | 0.05 | | | | |

a These are vendor recommendations. Some of these values have been exceeded in actual practice.

b Water should be chemically compatible with formation waters.

c The product of Mg as $CaCO_3$ x $SiO_2$ should be less than 35 000 mg/L.

d Total suspended solids in the recirculating water should be less than 200 mg/L.

Table 2 - Membrane performance at 1800 kPa and 24°C with dilute KI solution

| MEMBRANE NO.: | 1 | 2 | 3 | 4 | 5 | 6 |
|---|---|---|---|---|---|---|
| Material[a] | NC | PTFE | RC | NC | RC | CA |
| Pore size, m x $10^{10}$ | 100 | 200 | 50 | 50 | 50 | -[b] |
| Supplier | Sartorius | S and S[c] | S and S[c] | S and S[c] | S and S[c] | CANMET[d] |
| Heat treatment °C x 10 min | 80°C | 80°C | -[e] | 90°C | 80°C | -[e] |
| (PWP)[f], avg. g/h | 63.43 | 27.75 | 5.14 | 49.18 | 4.86 | 38.57 |
| (PR)[f,g], g/h | 63.09 | 24.94 | 5.35 | 50.15 | 5.04 | 37.94 |
| F[g], % | 7.3 | 7.3 | 12 | 12 | 20 | 32 |

[a]NC = Nitrocellulose; PTFE = Polytetrafluorethylene; RC = Regenerated Cellulose; CA = Cellulose Acetate.

[b] = undetermined

[c]S and S = Schleicher ans Schnell

[d]CANMET = Fabricated in-house

[e]No heat treatment was applied

[f]Surface area of $1.26 \times 10^{-3}$ $m^2$

[g]Calculated separation (eq 1) for a feed of 2050 ppm of KI

Table 3 - Analysis of permeate for the membranes of Table 2

| Membrane No. | 1 | 2 | 3 | 4 | 5 | 6 | Limit from Table 1 | Original[f] emulsion |
|---|---|---|---|---|---|---|---|---|
| Material/ Heat treatment | NC/ 80°C | PTFE/ 80°C | RC | NC/ 90°C | RC/ 80°C | CA | - | |
| 24°C Run | | | | | | | | |
| TDS, ppm[a] | 635 | 740 | 506 | 738 | 661 | 371 | 8 000 | 55 000 |
| Ca, ppm[b] | 0.07 | - | 0.07 | 0.07 | 0.07 | 0.07 | - | 1.8 |
| Mg, ppm[c] | 0.15 | - | 0.15 | 0.15 | 0.15 | 0.15 | - | 0.45 |
| Fe, ppm[d] | 0.12 | - | 0.12 | 0.12 | 0.12 | 0.12 | 0.05 | 4.7 |
| $SiO_2$, ppm | 63.3 | - | 59.8 | 63.2 | 56.6 | 39.4 | 50 | 157 |
| Suspended solids | no | no | no | no | no | no | 0 mg/L | yes |
| Suspended oil | no | no | no | no | no | no | 1.0 mg/L | yes |
| pH | 7 | 7 | 7 | 7 | 7 | 7 | - | 7 |
| Total hardness as $CaCO_3$ ppm[b] | 0.18 | - | 0.18 | 0.18 | 0.18 | 0.18 | 0.5 | 4.6 |
| Total organic carbon, ppm of C | 45.6 | 76.8 | 81.4 | 69.0 | 65.0 | 48.3 | - | 9 |
| 45°C Run | | | | | | | | |
| TDS, ppm[a] | 431 | NA | 771 | - | 755 | 173 | 8 000 | 55 000 |
| Ca, ppm[b] | 0.07 | 1.62 | 0.07 | - | 0.07 | 0.07 | - | 1.8 |
| Mg, ppm[c] | 0.15 | 0.52 | 0.15 | - | 0.17 | 0.15 | - | 0.45 |
| Fe, ppm[d] | 0.12 | 2.75 | 0.12 | - | 0.12 | 0.12 | 0.05 | 4.7 |
| $SiO_2$, ppm | 59.6 | 85.3 | 54.9 | - | 58.2 | 26.4 | 50 | 157 |
| Suspended solids | no | - | no | - | no | no | 0 mg/L | yes |
| Suspended oil | no | visible | no | - | no | no | 1.0 mg/L | yes |
| pH | 7 | 7 | 7 | - | 7 | 7 | - | 7 |
| Total hardness as $CaCO_3$, ppm[b] | 0.18 | 4.1 | 0.18 | - | 0.18 | 0.18 | 0.5 | 4.6 |
| Total organic carbon, ppm of C | 50.1 | - | 63.9 | - | 61.3 | 35.5 | - | 9 |

a TDS was calculated as residue at 90°C

b The minimum detectable limit for Ca is estimated to be 0.07 ppm. The corresponding limit for hardness as $CaCO_3$ is 0.175 ppm.

c The minimum detectable limit for Mg is estimated to be 0.152 ppm.

d The minimum detectable limit for Fe is estimated to be 0.118 ppm.

f Analysis by ICP on fused ash.

g Approximately 4% bitumen.

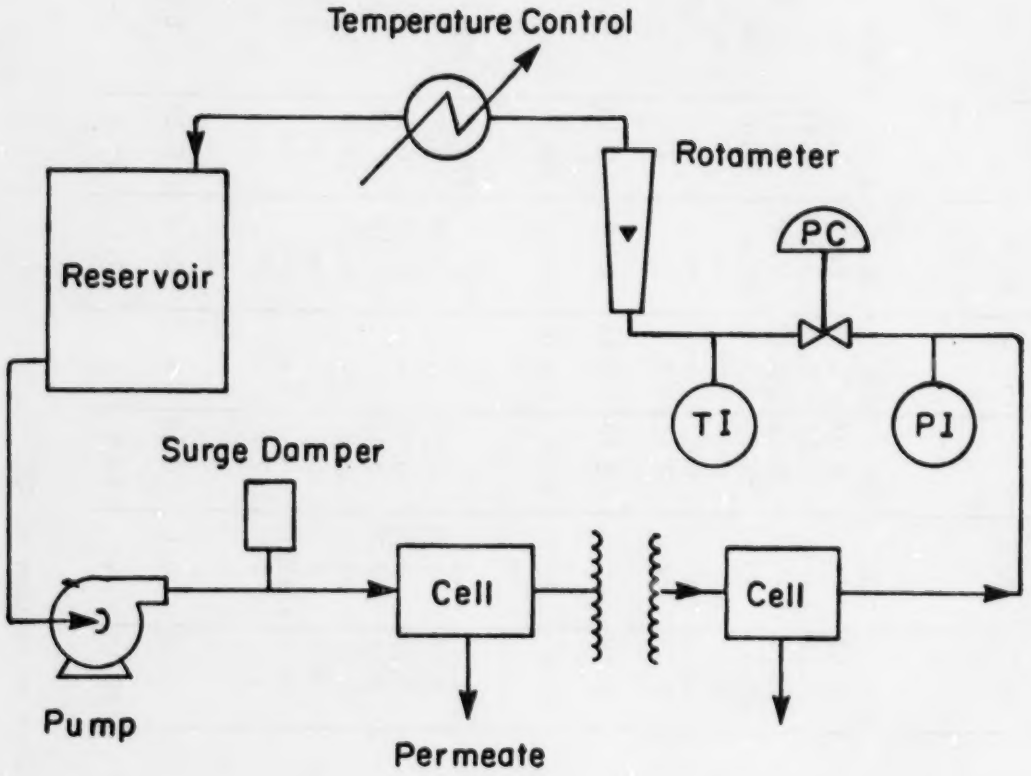


Fig. 1 - Continuous system for the evaluation of membrane performance.

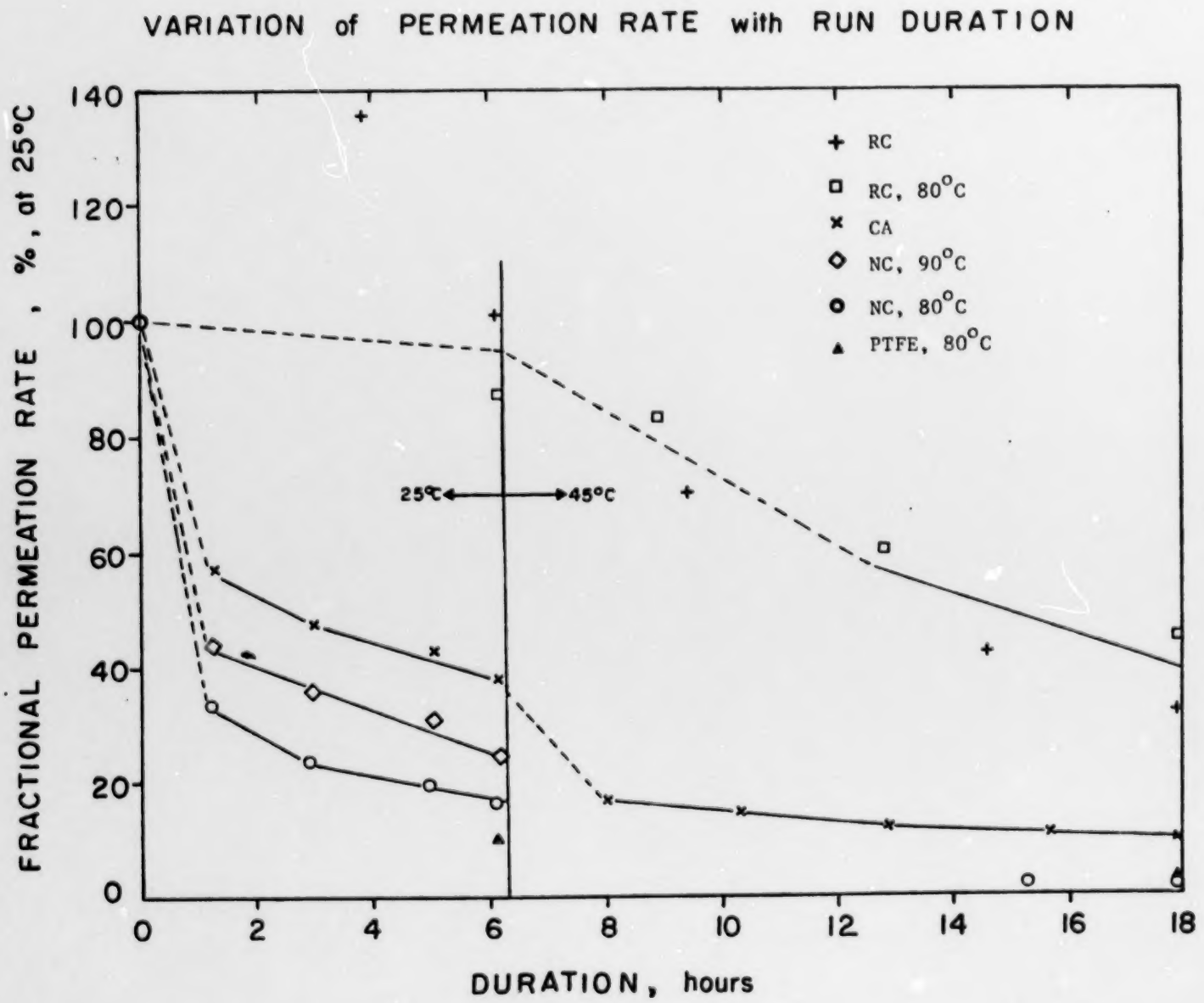


Fig. 2 - Variation of permeation rate with run duration.